Distorted perovskites for high voltage dielectric capacitors

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ABSTRACT

There are several mechanisms which have been proposed for the existence of colossal dielectric constant in the class of perovskite calcium copper titanate ($CaCu_3Ti_4O_{12}$ or CCTO) materials. Researches indicate that existence of twinning parallel to (100) (001) and (010) planes causes planar defects and causes changes in local electronic structure. This change can cause insulating barriers locally which contribute to the large dielectric values irrespective of processing. The combination of insulating barriers, defects and displacements caused by twinning have been attributed to the generation of large dielectric constant in CCTO. To examine some of these arguments some researchers replaced Ca with other elements and evaluated this concept. In this study we present the synthesis and characterization of $Ga_{2/3}Cu_3Ti_4O_{12-x}N_x$ (GCTON) material. This provides both distortion due to atomic size difference and defects due to insertion of nitrogen. The morphology of the compound was determined to show that processing has tremendous effect on the dielectric values. The resistivity of GCTON was several order higher than CCTO and dielectric constant was higher than 10,000.

Keywords: Dielectric, Capacitor, GCNTO, Resistivity, Grain, Annealing, Coarsening
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1. INTRODUCTION

Since the report of calcium copper titanate ($CaCu_3Ti_4O_{12}$ or CCTO) as a potential candidate for high dielectric capacitor material [1-4], a large number of researchers have performed extensive experiments on processing of CCTO and some other compounds of this class. These materials belong to body centered cubic structure with a slight tilt of $(TiO_6)^{-4}$ octahedrons facing each other. Several mechanisms have been proposed to explain the intrinsic high dielectric value in CCTO. Some authors have attributed the high dielectric constant to the grain boundaries and oxygen deficiencies. However, our extensive experiments have shown that dielectric constant was very much dependent on the processing and starting components. Although significant efforts have been devoted on the synthesis, growth of grains and characterization of $CaCu_3Ti_4O_{12}$ (CCTO) by Singh et al [2], practical low resistivity remains a big hurdle for its applications as a dielectric capacitor. It is expected that other members with perovskite structures will show the similar colossal dielectric constant. To achieve the goal of increased resistivity, deep level dopants and other small and large ion-based substitution process have been used. However, this challenging problem of low resistivity has not been resolved. It has been observed that morphology and dielectric values are very much dependent on the processing and process parameters. In this study we used lanthanum (Ga^{+3}) to replace calcium (Ca^{+2}). Also, instead of gallium oxide we used GaN as source material. This results in stoichiometry $Ga_{2/3}Cu_3Ti_4O_{12-\delta}N_\delta$ (GCTON). In another independent experiment, we used excess copper oxide to evaluate the effect of excess copper on dielectric values.

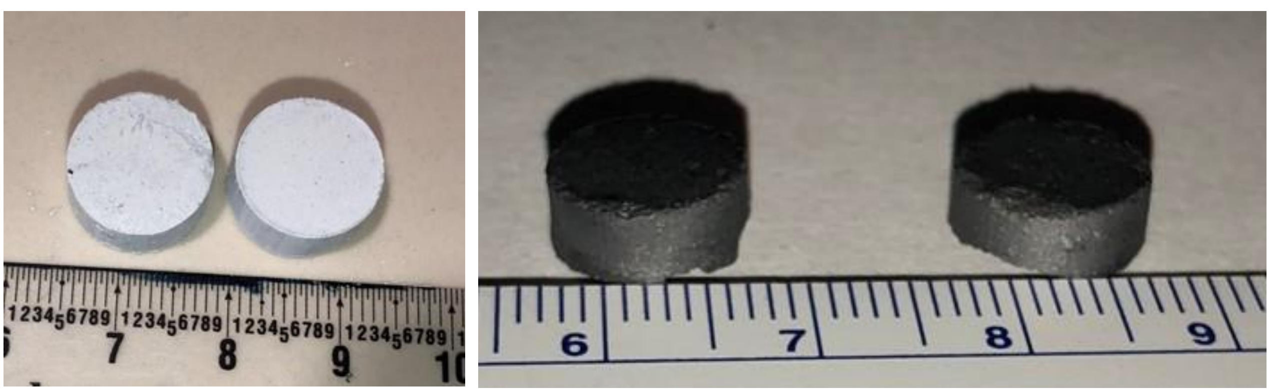
2. EXPERIMENTAL METHODS

2.1 Materials Synthesis: For the synthesis of stoichiometric $Ga_{2/3}Cu_3Ti_4O_{12-\delta}N_\delta$ (GCTON), we used GaN, CuO and TiO_2 to prepare the desired stoichiometry. Before preparing mixtures, we used Wig-L-bug to prepare the particles of uniform sizes of source materials. The particles sizes were in the range of 50 to 100μm size. Source materials were listed for 99.99+% purity. For the processing, powder was pressed to make pellets of cm sizes, using a pressure of 7000 to 8000 lb/inch^2. We used a temperature range of 600C for sintering and 950 ^{0}C for the grain growth, and at higher temperatures we observed partial melting and crystallization of the material. The morphology of material was studied by optical microscope and scanning electron microscope.

2.2 Fabrication and measurements of dielectric constant, capacitance and resistance: Details of parameters are described in references [3-5] for cutting, polishing, electrode bonding and other fabrication into capacitors. We were able to achieve good quality polished surfaces on polishers with pads and using several solvents. For most of the measurements we used silver paste for the electrode. However, we also tested the stability of gold electrodes. The material does not react with gold and long-term stability is extremely good. Parallel-plate capacitors were fabricated from pressed and sintered pellets with thicknesses from 0.5 to 2 mm (thinned and polished). Dielectric capacitance of bulk ceramic samples was inferred from measurement of complex impedance as a function of frequency from 001 to 1000KHz with an Agilent/HP 4284A LCR meter. Resistivity was inferred from two measurements: (a) using a parallel-resistance model of complex-impedance measurements and (b) measuring current from a dc voltage bias.

3.RESULT AND DISCUSSION

Most of the samples prepared in this study were in the range of 2.0 to 5 grams. The diameter was in the range of 7 to 10 mm. To prepare samples in this diameter range with few mm thickness, typical amount of each component GaN, CuO and TiO_2 was 0.506, 2.146 and 2.817 g. after crushing and mechanically mixing powder it was placed in wig-L-bug for grinding to make smaller size particles, The pressure applied in each case an identical pressure of 7500 to 8000 lb/inch^2 for pressing the samples. Typical as prepared samples of GCTON for sintering and annealed at 800C are shown in **Figure 1.** The sintering temperature of 600C showed significant shrinking and sintering. Grain growth was more visible above 800 ^oC. We did not observe much change in the morphology above 1080C. In the growth runs where we used excess copper oxide, we observed flow of copper rich phases around the pellet. In this case long needles or grains with large aspect ratio were observed. We observed that cracking was observed after a few hours of annealing at above 850 ^oC.



(a) **(b)**

Figure 1 (a) As prepared and (b) annealed at 800oC samples of GCTON

Silver dots were stable at room temperature. However, when sample was heated around 150C, silver dots showed spreading on the samples. **Figure 2-5** shows a typical morphology of grains with copper rich phases. These grains were facetted and had different sizes. It also shows that liquid drops were available between grains. Since copper oxide has the lowest constituent melting temperature, it starts melting well below the CCTO melting point, in contact with other constituents and starts flowing. When the sample was cooled down, copper rich material seggregated between the sintered grains**.** On some spots in the sample a thin layer of copper-rich oxide covered the grains. Unlike the case of CCTO, copper addition did not show any enhancement in grain growth. **Figure 4** shows a typical microstructure of GCTON after 50 hours of grain growth at 800^{o}C. It contained white residue in between grains. After 72 hours to 80 hours of annealing this residue disappeared and grains were much more homogeneous.

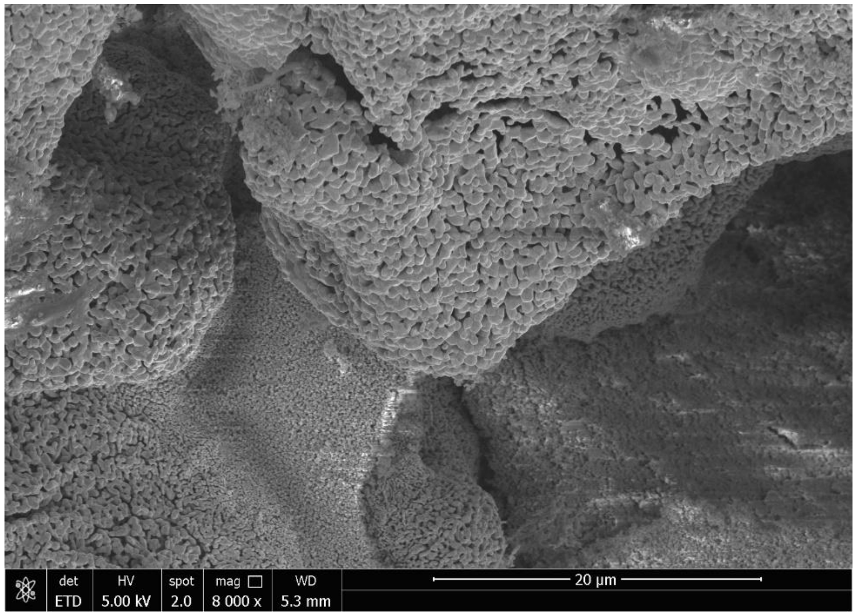


Figure 3. Morphology of GCTON grains showing elongated cells merging with side grains

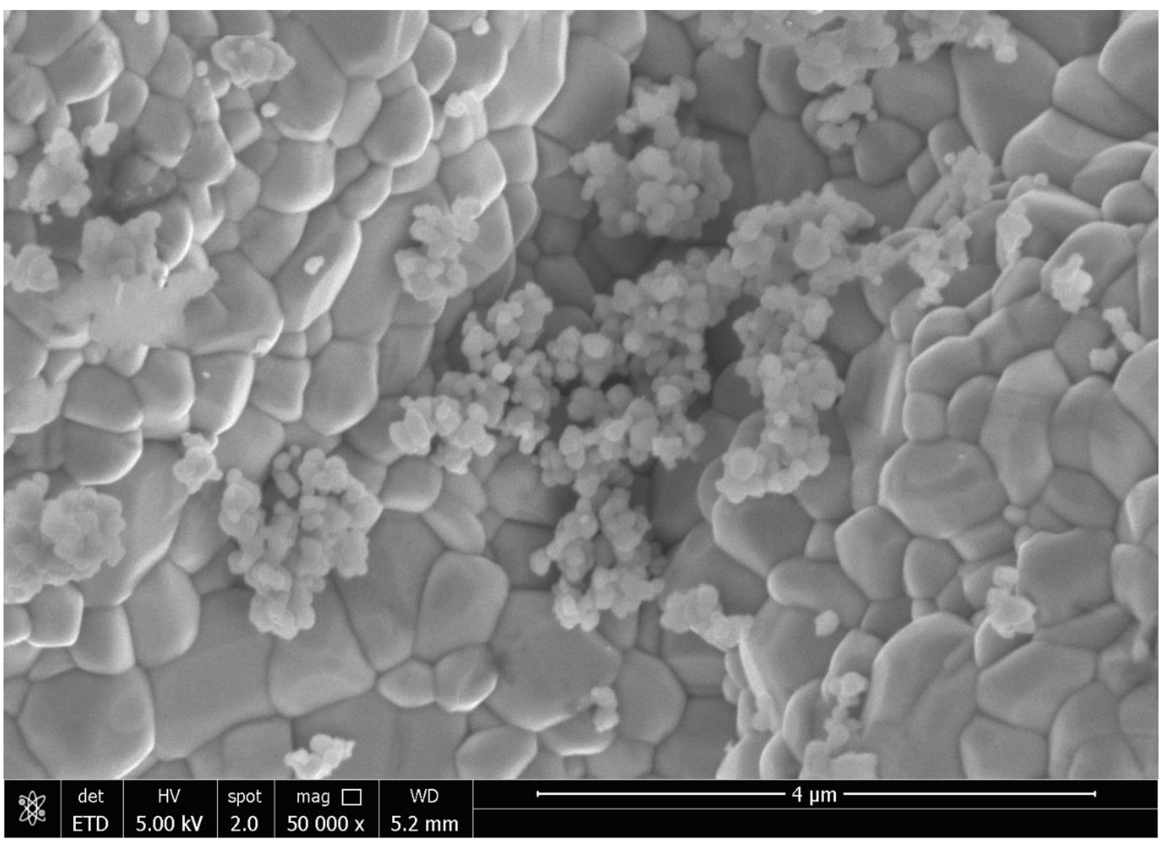


Figure 4. Morphology of sem ideveloped GCTON grains with 50 hours of growth showing residue on the surfaces of grains

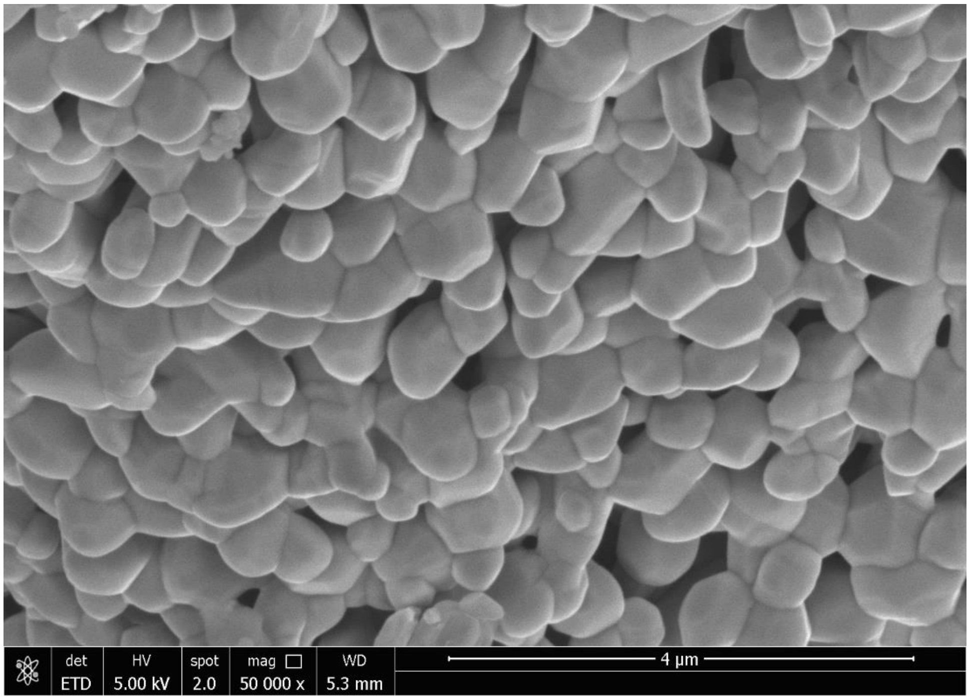


Figure 5. Morphology of grains after growth of 72-80 hours showing fully developed nonfacetted growth

Figure 4 shows that grains are very asymmetric and nonfacetted. In addition the mechanism of grain growth is very different than CCTO grains. All over the matrix it appears that elongated cells with small garins visible on the top of large grains. AS shown at several places, these small grains are sticking on larger grains and then disappearing to merge and form larger grains. From the reflection of the grains shown in **Figure 4** it is clear that smaller grains trapped, dissolved and larger grains grew in non-symmetric shapes. Most of the well-developed grains were elongated along certain orientation. As shown in **Figure 5** after 70-80 hours of grain growth larger grains were observed. These grains were less pointed but still had some smaller grains at the boundaries of larger grains. . This indicates that before complete mixing and forming stoichiometric GCTON, copper titanate in presence of GaN show some mixing to form small grains which slowly dissolves and forms grains with elongated shapes. We did not find faceting in the final GCTON morphology. This indicates that further merging of grains to grow larger grains may be possible. Then we took observations at various parts of the sample and it showed the same morphology. It appears that in some places, growth occurred quickly and grains grew in the range of few microns.

The dielectric constants of pure and doped GCTON were measured by processing 4.3 mm thick samples. We used silver paint electrodes on each side with electrode area ~ 1.8 mm^2. The highest value of capacitance and dielectric constant for a typical GCTON is shown in **Figures 6** and **7**. The highest value of LCTO at low frequency was in the range of 9000. The resistivity for pure LCTO was 3.8x 10^8 Ohm-cm. Very similar to that of CCTO material the dissipation generally given as Dissipation ≡ tan[Re Z(w)/Im Z(w)], is dominated by dc leakage current, not by the intrinsic tan delta (ac loss) of the capacitor dielectric. The details of this data are under measurements at Banaras Hindu University to explain the losses. The resistivity of the GCTON sample was several orders of magnitude higher than CCTO samples.

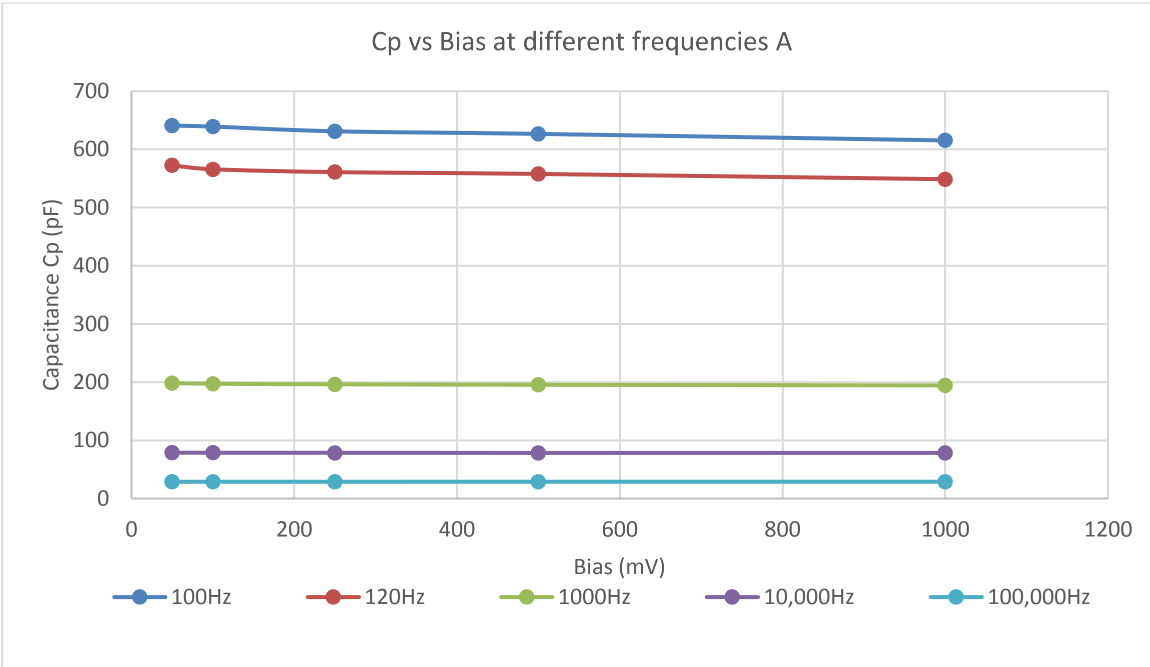


Figure 6. Capacitance of GCTON at different frequency and bias voltage

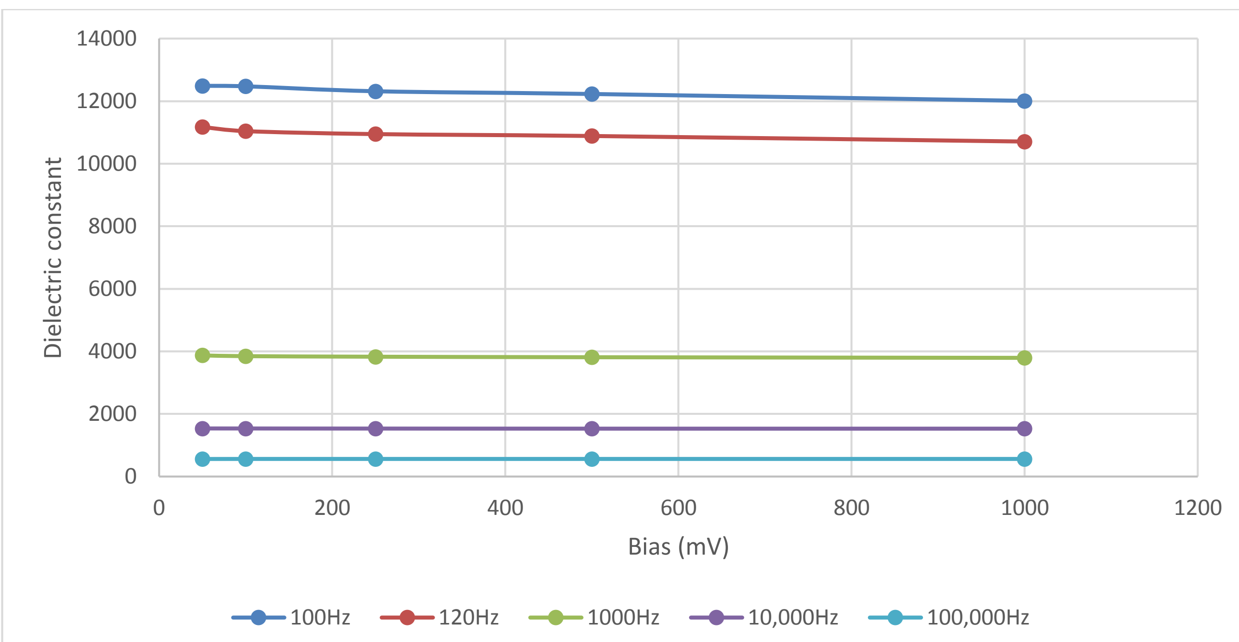


Figure 6. Dielectric constant of GCTON at different frequency and bias voltage

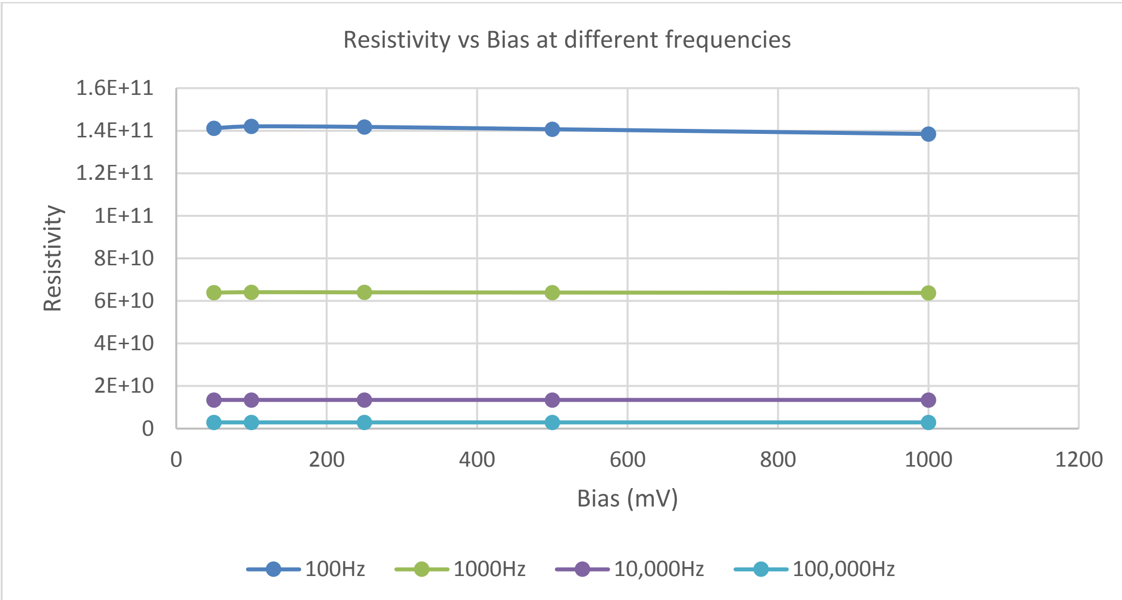


Figure 7. Resistivity of GCTON at different frequency and bias voltage

4. SUMMARY

To improve the resistivity of dielectric material, synthesis and grain growth of a novel material system with nonstoichiometric composition $Ga_{2/3}Cu_3Ti_4O_{12-\delta}N_\delta$ (GCTON) was performed to determine the effect of substitution in well studied $CaCu_3Ti_4O_{12}$ (CCTO) material system. Our results indicate that morphology and resistivity was very different. The resistivity was several order higher than CCTO and dielectric constant was >10,000. This shows that GCTON system is very attractive material system for practical dielectric storage. Experiments to evaluate effect of hetero valence and optimization of parameters for processing the material is continuing.

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5. REFERENCES

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